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Diagnostic implications of the reactivity of fluorescence tracers

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Figure 3: 485

Figure 4: 152

Figure 5: 156

Table 1: 456

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Abstract

Measurements of fuel concentration distributions with planar laser induced fluorescence of tracer molecules that are added to a base fuel are commonly used in combustion research and development. It usually is assumed that the tracer concentration follows the parent fuel concentration if physical properties such as those determining evaporation are matched. As an example to address this general issue a computational study of combustion of biacetyl/iso-octane mixtures was performed to investigate how well the concentration of biacetyl represents the concentration of iso-octane. For premixed mixture conditions with flame propagation the spatial concentration profiles of the two species in the flame front are separated by 110 μm at 1 bar and by 11 μm at 10 bar. For practical applications this spatial separation is insignificantly small. However, for conditions that mimic ignition and combustion in diesel and HCCI-like operation the differences in tracer and fuel concentration can be significant, exceeding hundreds of percent. At low initial temperature biacetyl was found to be more stable whereas at higher temperature ($>1000\text{K}$) iso-octane is more stable. Similar findings were obtained for a multi-component fuel comprised of iso-octane, n-heptane, methylcyclohexane, and toluene. It may be assumed that similar differences can exist for other tracer/fuel combinations. Caution has therefore to be applied when interpreting PLIF measurements in homogeneous reaction conditions such as in HCCI engine studies.

Keywords: LIF, fluorescence tracer, kinetic mechanism

Introduction

Optimized mixing of fuel and oxidizer is essential for improved combustion processes and in turn cleaner and more efficient combustion devices. It is therefore important to determine the status of mixing, local concentrations, gradients, and their temporal evolution. As most technical combustion processes are turbulent in nature such studies have to be performed with high temporal and spatial resolution. For experimental studies a common approach is to use planar laser induced fluorescence measurements to obtain maps of scalar quantities. Native combustion species like hydroxyl and methylidene radicals, nitric oxide can be directly measured. However, fluorescence tracers are typically necessary to measure distributions of parent fuels because common hydrocarbon fuels cannot be excited to produce fluorescence signals in practical situations. Given the importance of knowing the local fuel concentration the use of fluorescing tracers like ketones and aromatic molecules has gained large popularity. Those tracer molecules can be excited with lasers to produce signals that can be calibrated to deduce concentrations or temperature [1]. Toluene and 3-pentanone have been particularly popular in applications of planar laser-induced fluorescence (PLIF) fuel imaging in internal combustion engines. However, biacetyl has recently gained renewed interest due to its absorption in the near ultraviolet spectral region where it can be excited with high-repetition rate solid-state lasers [2].

The success of PLIF fuel imaging in research and development must not deter from the fact that there are a number of important aspects that have to be addressed in order to obtain reliable results from such measurements. Most important for the use of

fluorescence tracers is a proper understanding of the photo-physical response, i.e. how the absorption and fluorescence quantum yield of the tracer molecules depends on temperature, pressure and gas composition. There are also concerns about co-evaporation and diffusion of tracer and traced molecules that may be important under some experimental conditions [3-5]. If the tracer and base fuel are not properly matched in terms of evaporation dynamics the spatial distribution of tracer and base fuel may be different leading to unquantifiable errors in measuring the fuel distribution. This can be solved in some cases by considering the use of a blend of several tracers with overall evaporation characteristics that mimics that of the base fuel [3] or by considering the evaporation dynamics that shows that the relevance of sequential evaporation critically depends on the ambient pressure and temperature conditions [5]. Furthermore, it is important to ensure that the addition of tracer molecules does not alter the combustion process [6, 7], i.e., flame speed, etc. It has been shown for that toluene or 3-pentanone addition to iso-octane fuel has a small, negligible, effect on combustion performance with somewhat increasing impact towards leaner mixtures [7]. This suggests that care needs to be taken to match the equivalence ratio after adding the tracer and to ideally perform some baseline experiments to either rule out or at least quantify the impact of tracer addition on overall combustion performance, e. g. peak pressure value and timing in internal combustion experiments.

Lastly, the tracer chemistry must follow the chemical consumption rate of the traced molecules to guarantee a faithful measurement of the parent fuel concentration. Tait and Greenhalgh [8] have studied acetaldehyde to trace methane fuel in a diffusion flame and discussed application limits for that particular system. At high mixture fraction values the

acetaldehyde mole fraction was higher than that of methane but below mixture fractions of approximately 0.75 the acetaldehyde mole fraction was significantly below the methane levels. For practical, spatially resolved measurements this difference was judged to be insignificant and acetaldehyde was found to be a good tracer for methane as the parent fuel in nonpremixed flames. Reuss and Sick [9] used toluene in an n-heptane-fueled homogeneous-charge compression-ignition (HCCI) engine to investigate mixture homogeneity and the onset of reaction sites. The interpretation of the toluene fluorescence signal strength was ambiguous because of the uncharacterized role of toluene consumption in comparison to n-heptane breakdown under low-temperature combustion conditions. The onset of localized reaction sites was clearly identified by both a spatially identifiable decrease in toluene fluorescence strength and an increase in ensemble variation of the toluene signal. Through a comparison with pressure-based heat release analysis the changes could be linked with the increase in heat release. However, this is only indirect evidence that toluene tracked the consumption of n-heptane. For homogeneous reaction conditions where the fuel is consumed over time and no spatial variation occurs, the use of fluorescence tracers to track the fuel is especially problematic because the quantitative analysis of the measured signal strength now becomes even more critical. The observed reduction in toluene fluorescence signal at the onset of heat release could be attributed to either a the consumption of toluene or to a change in fluorescence yield due to local temperature changes since toluene fluorescence strength decreases with increasing temperature [9].

Experimental proof that the concentration of the base fuel is correctly tracked by a fluorescence tracer is not available. Direct species-specific measurements are difficult, especially in practical combustion devices such as internal combustion engines, unless, for example, spatially resolved probe measurements in low pressure flames coupled to gas chromatography or mass spectrometry would provide concentration profiles. While this would give information about premixed combustion with flame propagation, combustion conditions with significant low temperature chemistry, i.e. HCCI combustion, could not be addressed. Therefore, the current study focuses on numerical experiments where the combustion process of a fluorescence tracer and a base fuel is investigated with detailed chemical kinetic simulations.

A mixture of biacetyl and iso-octane was selected as the primary target system for this study. The use of biacetyl in high-speed imaging studies makes it an important fluorescence tracer to characterize. However, it has to be emphasized that this combination of tracer and fuel is just chosen as an example to illustrate the overall problem of tracer reactivity and its impact on quantitative scalar measurements in reacting flows. Detailed reaction mechanisms are available for the combustion of iso-octane, a widely used surrogate fuel for gasoline in numerical and experimental work. We have used the iso-octane mechanism of Curran et al.[10], but it was necessary to develop a new kinetic mechanism for biacetyl, which has not previously been a subject of kinetic modeling research.

A matrix of combustion conditions was chosen to address situations of practical relevance for engine and other possible environments. Premixed flame front propagation, important in spark-ignition engines, and compression-ignition, important in diesel and HCCI engines, were both studied numerically. Flame propagation was examined at atmospheric temperature and pressure and at 10 bar pressure and unburned gas temperature of 600K. In addition, homogeneous autoignition was examined at 5 bar initial pressure and temperatures from 800K to 1300K. In the flame simulations, the impact of molecular diffusion of the fuel was examined by varying the diffusion coefficient of biacetyl, and propane was substituted for iso-octane to investigate the influence of a different fuel. In the homogeneous autoignition conditions, another surrogate for gasoline was also studied, consisting of a multi-component mixture of species, to examine the role of differences in hydrocarbon consumption chemistry. This surrogate fuel contains toluene so that the results of this computation can also serve towards an evaluation of the importance of toluene reactivity in imaging experiments.

Computational Approach

Laminar flame calculations and homogeneous reactor simulations were carried out using the Chemkin 4.1 model [11] and the HCT model [12], using kinetic reaction mechanisms as described below.

Iso-Octane

The calculations were carried out using the iso-octane kinetic mechanism of Curran et al. [10], which has been validated thoroughly through comparisons between experimental

and computed results. Most important, these validation studies covered wide ranges in equivalence ratio, temperature, and pressure, in experimental regimes including laminar flames, shock tubes, rapid compression machines, and stirred and static reactors. In addition, the same mechanism has been used in many engine studies of spark-ignition and HCCI combustion.

The mechanism shows that the most important reactions consuming iso-octane consist of H atom abstraction from the fuel, followed by iso-octyl radical decomposition at high temperatures and addition of molecular oxygen and alkylperoxy radical isomerization reactions at lower temperatures. Thermal decomposition of iso-octane competes with H atom abstraction for fuel consumption at high temperatures.

An important feature of iso-octane molecular structure is that it includes primary, secondary and tertiary C - H bonds. Primary C - H bonds have strong bond energies, secondary C - H bonds are weaker, and tertiary C - H bonds are even weaker, so at low reaction temperatures where only the weakest C - H bonds can be broken, rates of iso-octane consumption are faster than in fuels that have no secondary or tertiary C - H bonds. Another important feature of iso-octane is that it produces large amounts of isobutene, which is relatively unreactive and slows the subsequent overall rate of reaction.

Biacetyl reaction mechanism

Biacetyl ($C_4H_6O_2$) has not been studied previously in kinetic models and it is not included within kinetic mechanisms of larger fuel molecules, so a new mechanism for its oxidation was required. The molecule itself consists of two acetyl radicals, joined by a C - C bond. As a result of this structure, all 6 H atoms are bound at primary C - H sites, so their bond energies are quite strong and are relatively difficult to abstract. However, at high temperatures, the biacetyl species is relatively unstable and decomposes quite rapidly into two acetyl (CH_3CO) radicals, which rapidly decompose further into CH_3 and CO. In addition, H atom abstraction from biacetyl produces the $CH_3COCOCH_2$ radical which decomposes rapidly into ketene and acetyl, both of which are quite reactive.

Rates of H atom abstraction in biacetyl by radicals were estimated as equal to abstraction rates of primary H atoms in propane and similar species. Rates of decomposition reactions were determined by specifying the addition rates of radicals to produce biacetyl, and then computing the decomposition reaction rates using microscopic reversibility. Thermochemical quantities for biacetyl and its related radicals were computed using the THERM software [13] of Ritter and Bozzelli. The biacetyl submechanism is summarized in Table 1.

Additional kinetic mechanisms

In addition to iso-octane/biacetyl mixtures, laminar flame calculations were carried out using mixtures of propane and biacetyl as fuel. A submechanism for propane developed by Petersen et al. [14] was used for the propane flame calculations, coupled to the new biacetyl mechanism. In addition to the iso-octane/biacetyl mixtures, homogeneous

ignition calculations were also carried out for a surrogate gasoline mixture including toluene [15], methylcyclohexane [16], n-heptane [17] and iso-octane with biacetyl, using submechanisms for each component that have been developed previously.

Results

Propagating flames

Stoichiometric, laminar, premixed flame models were computed for fuel/air at one and 10 bar pressure, with the fuel consisting of 90% iso-octane and 10% biacetyl. The temperature, iso-octane, and biacetyl spatial profiles for these two flames are plotted in Figures 1 and 2. The following observations can be made from these profiles with respect to the analysis of PLIF images. At a flame front, fluorescence tracer images of fuel distributions typically show a clearly delineated border where the tracer disappears [18]. PLIF images are usually acquired with laser sheet illumination where the thickness of the laser sheet is a few hundred micrometers. The temperature profile shown in Fig. 1 indicates that under atmospheric conditions the flame front is approximately 1 mm thick. The iso-octane fuel concentration drops from its initial value to negligible levels within less than half that distance. Resolving this gradient is challenging in most experimental setups based on the thickness of the laser sheet, and at least some convolution of the measured gradient and the detection function is expected. This compares to a spatial separation of the biacetyl and iso-octane profiles within the flame front of just 110 μm , measured at the 50% level of the initial biacetyl concentration. For combustion under higher pressure conditions typical of internal combustion engines or gas turbines the flame front thickness decreases significantly and the spatial separation of the biacetyl and

iso-octane concentrations is only 11 μm at 10 bar (Figure 2). For all practical purposes this separation is too small to be measured and would be even smaller for pressures higher than 10 bar.

For these computations, the biacetyl diffusion coefficient was estimated from the square of the ratio of molecular weights of biacetyl and iso-octane, $(86/114)^{0.5} \approx 0.87$. To address the significance of molecular diffusion on the concentration profiles, this ratio was artificially reduced to 0.5 to exaggerate differences between the rates of tracer and fuel molecule diffusion. The spatial separation of biacetyl and iso-octane remained unchanged at 11 μm .

An additional laminar premixed, stoichiometric, atmospheric pressure propane/biacetyl/air flame was modeled, in which the spatial separation of propane and biacetyl profiles was calculated to be approximately 120 μm , only slightly larger than in the corresponding iso-octane/biacetyl flame. Similar to the case of iso-octane, the flame thickness and the separation between the fuel and biacetyl species profiles decreases significantly to levels that cannot realistically be measured experimentally as pressure increases to 10 bar and higher values.

In a laminar premixed flame, fuel is consumed primarily by H atom abstraction reactions, mostly by small, highly diffusive radicals such as H, O, OH and HO₂. As noted above, rates of H atom abstraction are fastest for H atoms bound at tertiary C sites in the fuel, slowest for H atoms bound at primary sites, with abstraction at secondary sites at

intermediate rates. Iso-octane, with its tertiary and secondary C - H bonds, begins to be consumed earlier in the flame at lower local temperatures than biacetyl, which has exclusively primary C - H bonds. This effect is not especially strong, since only 3 of the 18 C-H bonds in iso-octane have these lower C - H bond strengths, so the differences in fuel consumption and species fronts between iso-octane and biacetyl are not large, resulting in the very small distances between these profiles in Figs. 1 and 2. For measurements in combustion environments in which combustion takes place via flame propagation, biacetyl appears to be a reliable surrogate for iso-octane and other hydrocarbon fuels in identifying concentrations and rates of combustion.

Homogeneous reaction conditions

Computations were carried out to simulate conditions relevant to HCCI and diesel ignition, using an adiabatic reactor model with an initial pressure of 5 bar and initial temperatures from 800K to 1300K. Each case has 1% fuel, 12.5% O₂ and 86.5% N₂. As for the premixed flame computations, the fuel consists of 90% iso-octane and 10% biacetyl (i.e., 1000 ppm), a value typically chosen for experimental work to obtain acceptable fluorescence signal levels. The fuel/oxygen ratio is stoichiometric when the fuel is iso-octane, and when 10% of the iso-octane is replaced by biacetyl, the overall equivalence ratio changes slightly, to $\phi = 0.93$ [7], resulting in a small reduction in the ignition delay time, relative to pure iso-octane fuel, at a given initial temperature and pressure.

For these iso-octane/biacetyl mixtures, as the initial temperature T_o increases from 800 K to 1300 K to represent the range typically found in HCCI engines, the computed ignition delay decreases from about 0.65 seconds at $T_o = 800\text{K}$ to 45 ms at $T_o = 900\text{K}$, to 3 ms at $T_o = 1100\text{K}$ and 0.2 ms for $T_o = 1300\text{K}$. Pulsed laser based measurements can easily take snapshots within 10 ns or even less and can therefore capture the instantaneous tracer concentration. High-speed imaging capability will even allow capturing sequences within a given combustion event. However, if the tracer decomposes at a different rate than the fuel, it may not be possible to deduce the actual fuel concentration unless additional information about the local reaction conditions is available. This is in contrast to the results shown for flame propagation, where the small spatial difference between tracer and fuel concentration profiles observed in the computations could only be detected with the most sophisticated optical setups and will in practice be negligible.

The computational results for the adiabatic reactor calculations show that the iso-octane fuel is consumed more rapidly than the biacetyl fluorescence tracer at the lower initial temperatures of 800K and 900K. The opposite trend is found for initial temperatures of 1100 and 1300K, showing more rapid consumption of biacetyl than for iso-octane. Figure 3 shows a series of normalized concentration plots and temperatures computed for these initial temperatures. In each case, concentrations of both iso-octane and biacetyl decrease steadily until the time of ignition when both have been completely consumed. It is also evident that, for nearly all this ignition delay time, and for every initial temperature, the normalized fuel and tracer concentrations are not the same, and these differences vary with temperature in a complex manner.

Some of the differences in relative consumption rates of iso-octane and biacetyl at different temperatures can be understood by relating them to the laminar premixed flames described earlier. At the lower temperatures of 800K and 900K, fuel consumption takes place almost entirely by means of H atom abstraction as in the laminar flames. Because iso-octane has secondary and tertiary C - H bonds, those H atom abstraction reactions are faster for iso-octane than for biacetyl with only primary C - H bonded H atoms and iso-octane is consumed more rapidly than biacetyl.

At the higher temperatures of 1100K and above, the entire nature of the ignition changes from that at lower temperatures. Unimolecular decomposition of the fuel becomes an important reaction pathway, and these decomposition reactions are quite endothermic, producing the initial decrease in mixture temperatures that can be seen in Fig. 3c and 3d. The increasing role of the decomposition reaction as temperature increases is particularly evident from the much greater initial drop ($\sim 15\text{K}$) in temperature in the 1300K case (Fig. 3d) than the approximately 2K drop in the 1100K case (Fig. 3c). At these elevated temperatures, there is less difference between H abstraction rates at primary, secondary and tertiary sites, so the preference for H abstraction in iso-octane observed at lower temperatures disappears.

If the normalized concentration of the tracer is used to determine the amount of iso-octane fuel at any given time in these homogeneous autoignition environments, these curves show that such a measurement can yield significant errors. Errors in the fuel

concentration as measured via the tracer signal in this way can reach hundreds of percent. These trends are particularly complex, since the higher reactivity of iso-octane relative to biacetyl varies with temperature and then reverses at some temperature, so it will be difficult to quantitatively analyze PLIF images unless the complete temperature history of the reactive mixture is known. It also must be noted that changing the stoichiometry of the initial mixture or adding exhaust gas to the unburned charge will also change the relationship between fuel and tracer concentration.

A thermal autoignition calculation was carried out in which the iso-octane fuel was replaced by a multicomponent mixture of n-heptane (1800 ppm), toluene (900 ppm), iso-octane (3600 ppm), and methyl cyclohexane (2700 ppm), combined with 1000 ppm of biacetyl, with 12.5% O₂ and 86.5% N₂. The computed results at 5 bar pressure and initial temperature of 1300K are shown in Figure 4, and the time scale for reaction of iso-octane and biacetyl is virtually identical to that when only iso-octane and biacetyl are present in the fuel, as shown in Fig. 3d for an initial temperature of 1300K. Interestingly, all of the other three components are consumed more slowly than either biacetyl or iso-octane under these conditions, so biacetyl would be an even worse predictor of their relative concentrations than for iso-octane.

The impact of the tracer addition on ignition delay was investigated with a set of computations that determined the thermal autoignition delay at a fixed starting condition of 1100 K and 5 bar for the pure fuel, a 90% fuel/10% biacetyl mixture, and the pure tracer. Iso-octane and the 5-component surrogate fuel were investigated. Figure 5 shows that the ignition delay of pure biacetyl is significantly shorter than that of the pure fuels.

The addition of 10% biacetyl to either of the fuels results in a significant reduction of the ignition delay. This finding falls in line with the observation that the consumption rate of biacetyl is higher than that of the hydrocarbon fuel as shown in figures 3c and 4. The data shown in figures 3 a and b shows that at lower temperatures biacetyl reacts more slowly than the fuel. Thus, it can the impact of biacetyl addition on ignition delay will be small, given that there are only 10% biacetyl in the mixture.

Conclusions

Measurements of fuel concentration distributions, using planar laser induced fluorescence of tracer molecules that are added to a base fuel, are commonly used in combustion research and development. It usually is assumed that the tracer concentration follows the parent fuel concentration if physical properties such as those determining evaporation or mixing are matched. Frequently used tracers often are small organic molecules such as toluene, acetone, 3-pentanone, and for recent high-speed imaging work biacetyl has gained renewed interest. A computational study of combustion of biacetyl/iso-octane mixtures as well as a multicomponent fuel has been performed as an example to investigate how well the concentration of a tracer represents the concentration of the base parent fuel. For premixed mixture conditions with flame propagation, the spatial concentration profiles of the two species are closely coupled and measureable differences are only expected at atmospheric pressure conditions and below, using very high resolution imaging setups. The spatial separation of biacetyl and iso-octane profiles in the flame front is about 110 μm , and this distance drops to 11 μm at 10 bar. For practical applications and especially in technical devices these differences are not resolvable. However, for conditions that mimic the combustion process in diesel and HCCI-like operation the differences in tracer and fuel concentration can be significant, exceeding hundreds of percent. Investigations of biacetyl/iso-octane and biacetyl/multi-component fuel, including toluene, show similar results. The different fuel components in HCCI seem to track each other in the sense that they all disappear over the same time interval,

but their rates of consumption are not proportional. However, they all seem to disappear at about the same time, which is effectively the time of autoignition.

At low initial temperature, biacetyl was found to be more stable whereas at higher temperature ($>1000\text{K}$) iso-octane is more stable. It may be assumed that similar differences can exist for other tracer/fuel combinations as a brief investigation of biacetyl/propane mixtures shows. Low temperature, alkylperoxy radical isomerization reaction pathways have not been emphasized in the present model calculations, but they are expected to present further complications in homogeneous autoignition conditions. Overall, the interpretation of concentration measurements based on the use of fluorescence tracers may be very difficult, particularly in cases where the fuel and the tracer exhibit significantly different levels of low temperature reactivity. This will be particularly true if the local temperature is not known. Caution has therefore to be applied when interpreting PLIF measurements in HCCI engine studies. When detailed reaction mechanisms exist for both the fuel and the tracer, computational modeling may be able to assist in relating the tracer and the main fuel.

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Tables

Reaction	log A	n	Ea (cal/mol)
$(\text{CH}_3\text{CO})_2 + \text{H} = \text{CH}_3\text{COCOCH}_2 + \text{H}_2$	13.27	0.0	6357
$(\text{CH}_3\text{CO})_2 + \text{OH} = \text{CH}_3\text{COCOCH}_2 + \text{H}_2\text{O}$	12.00	0.0	1192
$(\text{CH}_3\text{CO})_2 + \text{O} = \text{CH}_3\text{COCOCH}_2 + \text{OH}$	13.00	0.0	5962
$(\text{CH}_3\text{CO})_2 + \text{HO}_2 = \text{CH}_3\text{COCOCH}_2 + \text{H}_2\text{O}_2$	4.68	0.0	14690
$(\text{CH}_3\text{CO})_2 + \text{O}_2 = \text{CH}_3\text{COCOCH}_2 + \text{HO}_2$	13.62	0.0	49150
$(\text{CH}_3\text{CO})_2 + \text{CH}_3 = \text{CH}_3\text{COCOCH}_2 + \text{CH}_4$	11.50	0.0	9630
$(\text{CH}_3\text{CO})_2 + \text{CH}_3\text{O} = \text{CH}_3\text{COCOCH}_2 + \text{CH}_3\text{OH}$	11.64	0.0	4660
$(\text{CH}_3\text{CO})_2 + \text{CH}_3\text{O}_2 = \text{CH}_3\text{COCOCH}_2 + \text{CH}_3\text{O}_2\text{H}$	12.78	0.0	17580
$\text{CH}_3\text{CO} + \text{CH}_3\text{CO} = (\text{CH}_3\text{CO})_2$	12.00	0.0	0
$\text{CH}_3\text{COCOCH}_2 + \text{H} = (\text{CH}_3\text{CO})_2$	13.00	0.0	0
$\text{CH}_3\text{COCOCH}_2 = \text{CH}_3\text{CO} + \text{CH}_2\text{CO}$	13.20	0.0	30000

Table 1. Submechanism for biacetyl oxidation. Units are cal/mol, cm, s.

List of Captions for the Figures

- Figure 1: The biacetyl concentration follows the iso-octane parent fuel concentration in a premixed iso-octane/biacetyl/air flame at 1 bar and 300K initial temperature with a spatial shift of 110 μm .
- Figure 2: The biacetyl concentration follows the iso-octane parent fuel concentration in a premixed iso-octane/biacetyl/air flame at 10 bar and 600K initial temperature with a spatial shift of 11 μm .
- Figure 3: Under homogeneous reaction conditions biacetyl and iso-octane exhibit strongly different temporal concentration profiles that critically depend on initial conditions. At lower initial reaction temperatures of 800K (a) and 900K (b) biacetyl is more stable than iso-octane whereas the opposite is found at 1100K (c) and 1300K (d). The initial pressure was set to 5 bar.
- Figure 4: All components of a multi-component gasoline surrogate fuel react more slowly than biacetyl when the reaction is initiated at 1300K and 5 bar.
- Figure 5: The addition of 10% biacetyl to the base fuels decreases the autoignition delay significantly. The data shown were obtained for starting conditions of 1100K and 5 bar.

Figures.

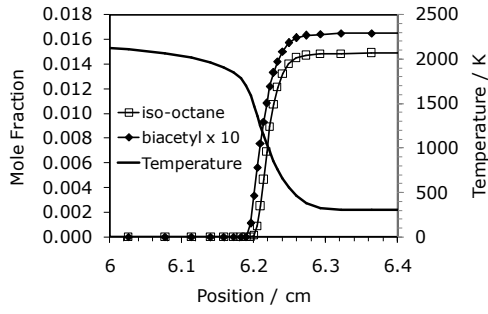


Figure 1: The biacetyl concentration follows the iso-octane parent fuel concentration in a premixed iso-octane/biacetyl/air flame at 1 bar and 300K initial temperature with a spatial shift of 110 μm .

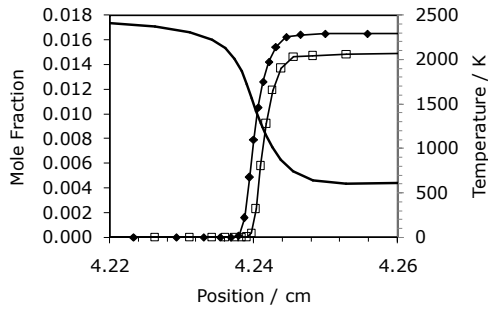


Figure 2: The biacetyl concentration follows the iso-octane parent fuel concentration in a premixed iso-octane/biacetyl/air flame at 10 bar and 600K initial temperature with a spatial shift of 11 μm .

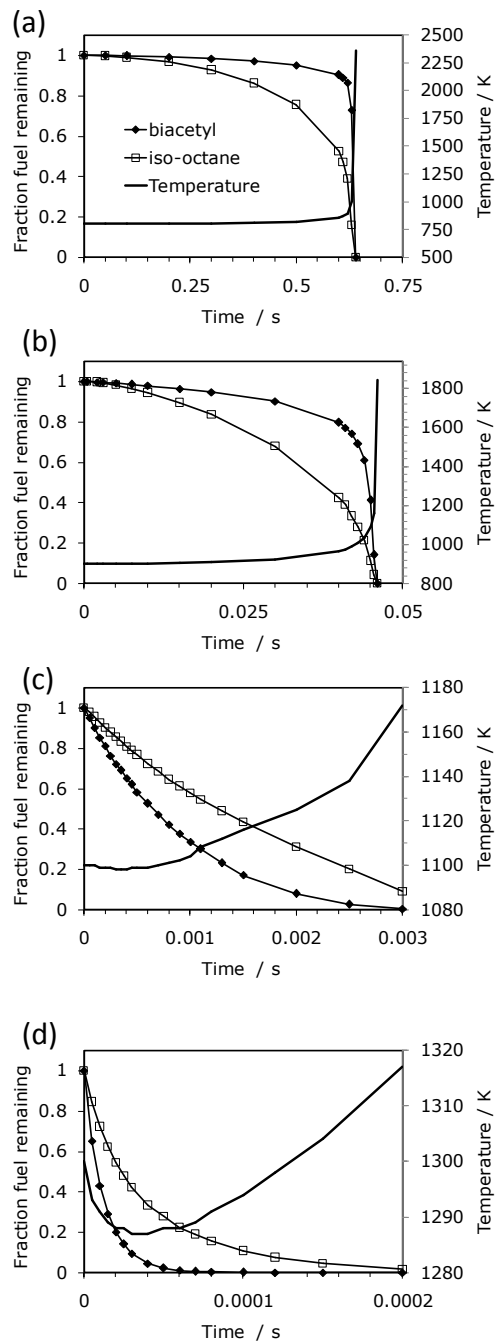


Figure 3: Under homogeneous reaction conditions biacetyl and iso-octane exhibit strongly different temporal concentration profiles that critically depend on initial conditions. At lower initial reaction temperatures of 800K (a) and 900K (b) biacetyl is more stable than iso-octane whereas the opposite is found at 1100K (c) and 1300K (d). The initial pressure was set to 5 bar.

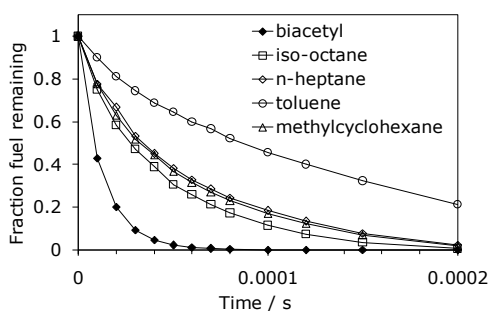


Figure 4: All components of a multi-component gasoline surrogate fuel react more slowly than biacetyl when the reaction is initiated at 1300K and 5 bar.

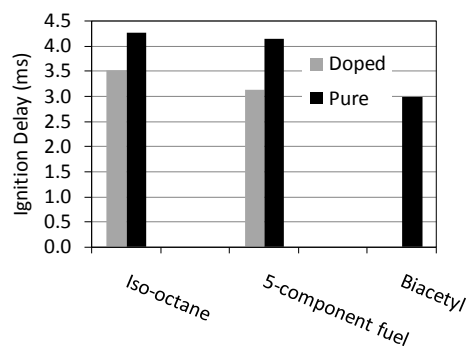


Figure 5: The addition of 10% biacetyl to the base fuels decreases the autoignition delay significantly. The data shown were obtained for starting conditions of 1100K and 5 bar.